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(54) **Thermographic material.**

(57) Images are formed by directing radiation, such as red or infra-red laser light, at a radiation sensitive plate and modulating the radiation. The radiation-sensitive plate includes a coating comprising coreshell particles having a water insoluble heat softenable core component and a shell component which is soluble or swellable in aqueous alkaline medium. The radiation causes selected particles to coalesce, at least partially, to form an image and the non-coalesced particles are then selectively removed by means of an aqueous alkaline developer.

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This invention relates to image formation and is concerned with the formation of images directly from electronically composed digital sources.

For many years it has been a long term aim in the printing industry to form printing images directly from an electronically composed digital database i.e. by a so-called "computer-to-plate" system. The advantage of such a system over the traditional methods of making printing plates are:-

- (i) the elimination of the costly intermediate silver film and processing chemicals
- (ii) a saving of time, and
- (iii) the ability to automate the system with consequent reduction in labour costs.

The introduction of laser technology provided the first opportunity to form an image directly on a printing plate by directing a laser beam at sequential areas of the plate and modulating the beam so as to vary its intensity. In this way, radiation sensitive plates comprising a high sensitivity photocrosslinkable polymer coating have been exposed to water cooled UV argon-ion lasers and electrophotographic plates having sensitivity stretching from the visible spectral region into the near infra-red region have been successfully exposed using low powered air-cooled argon-ion and semiconductor laser devices.

Imaging systems are also available which involve a sandwich structure which, on exposure to a heat generating infra-red laser beam, undergoes selective (image-wise) delamination and subsequent transfer of materials. Such so-called peel-apart systems are generally used as replacements for silver halide films.

According to one aspect of the present invention there is provided a radiation sensitive plate which comprises a substrate coated with (i) one or more layers each comprising core-shell particles each of which comprises a water-insoluble heat softenable core component (A) and a shell component (B) which is soluble or swellable in aqueous alkaline medium, and (ii) a substance capable of strongly absorbing radiation and transferring the energy thus obtained as heat to the core-shell particles so that at least partial coalescence of the particles occurs.

The plate may contain one or more additional layers so as to increase adhesion to the substrate, improve resistance to abrasion, or to improve the performance of the system in other respects.

According to another aspect of the present invention there is provided a method of forming an image which comprises

- (a) providing a radiation sensitive plate as hereinabove defined,
- (b) image-wise exposing the radiation-sensitive plate to a beam of high intensity radiation, by directing the radiation at sequential areas of the coating and modulating the radiation so that the particles in the coating are selectively at least partially coalesced, and

(c) developing the image-wise exposed plate with aqueous alkaline medium to selectively remove the areas containing the non-coalesced particles and leave an image on the substrate resulting from the at least partially coalesced particles.

It may be desirable to increase the degree of coalescence of the selectively coalesced core-shell particles or to increase the adhesion of the image to the substrate. This may be achieved after the selective removal of the non-coalesced particles by heating the plate to a temperature, and for a time, sufficient to further soften or melt the particles, and to bring about the desired effect.

The substrate material used depends upon the purpose for which the image is to be used and may be, for example, formed of metal or plastics material. In the case where the image is to be used as a printing image, the substrate is preferably electrochemically treated aluminium whereas the substrate may be a linear polyester in the case where a transparency is to be produced or copper in the case where the image is to be used in printed circuit board manufacture.

The core-shell particles contain distinct domains of components (A) and (B). The domains are arranged so that component (A) (the core) is encapsulated by component (B) (the shell) with the core and shell being linked to each other by strong physical adsorption or, more preferably, by chemical bonding. Under ambient conditions, both components are preferably solid and immobile. As a generality, core-shell particles are known and methods for preparing the same are described in US patent specification No.4868016 and in British patent specifications No.887356 and No.1107249 (Example 22).

The component (A) is an oleophilic polymer, preferably having a minimum film forming temperature (MFT) above ambient temperature, and may be an addition polymer comprising residues derived from one or more of styrene, substituted styrenes, esters of (meth)acrylic acid, vinyl halides, (meth)acrylonitrile, vinyl esters or polyethers, or it may be a polyester, polyamide or polyurethane, or any thermally fusible oleophilic material or composition capable of forming a core-shell structure as defined above. Preferred materials are addition polymers containing 50% or more by weight of styrene or substituted styrenes.

The component (B) is preferably polymeric and contains carboxylic acid, sulphonamido, or other groups capable of conferring solubility, or at least swellability, in aqueous alkaline solutions. Particularly suitable materials for component (B) are: i) copolymers derived from the copolymerisation of one or more ethylenically unsaturated carboxylic acids with one or more of styrene, substituted styrenes, (meth)acrylate esters, (meth)acrylonitrile or vinyl acetate; ii) dicarboxylic acid half-esters of hydroxyl group-containing polymers, such as phthalic, succinic or maleic acid half esters of a polyvinyl acetal and, in

particular, of a polyvinyl butyral; and iii) alkyl or aralkyl half esters of styrene- or alkyl vinyl ether-maleic anhydride copolymers, in particular alkyl half esters of styrene-maleic anhydride copolymers such as Scripset 540 (Monsanto).

The shell component of the core shell polymer is used as the film forming component in the imaging layer, but also fulfils a vital role in stabilising the polymer particles, both when in aqueous dispersion during coating of the substrate and when in the imaging layer on the substrate. Thus the shell component may function as a protective colloid during the preparation of component (A) using an emulsion polymerisation process whereby little or no surfactant is necessary, or alternatively may colloiddally stabilise polymer particles which have been preformed with insufficient surfactant to ensure stability. For example, polystyrene prepared using 2% by weight of monomer of sodium lauryl sulphate is not storage stable in aqueous dispersion, but becomes stable when component (B), functioning as a protective colloid is added. Component (B) then subsequently acts as a film forming component in the imaging layer.

Where a two stage or inverse core shell polymerisation method is used as, for example, described in European Patent Publication No. 338486, the hydrophobic core particles can be stabilised by the shell when this is carboxyl functional either in the neutralised or unneutralised state. It is preferred that no carboxyl monomer is used in the core component as this can result in overdevelopment.

The shell component will generally film form preferentially to the core component either by virtue of it having a lower MFT or by virtue of, for example, it having been solubilised by a volatile base such as ammonia.

It is particularly important that the shell component is non-water soluble. Although the shell component contains such groups as carboxyl and sulphonamido, which confer the required solubility or swellability in aqueous alkaline solution, it is not soluble in water *per se* and, when cast down as a component of the heat sensitive layer in accordance with the invention, it does not impart to that layer a sensitivity to water. A marked deterioration in the properties of these films occurs when water soluble materials, including surfactants, are present at levels over a low threshold value. Amongst the problems caused by the presence of water-soluble components are the following:

1. The plates become sensitive to finger contact and to water.
 2. The storage stability, especially under humid conditions, deteriorates markedly.
 3. Adhesion of the coating to metal substrates is reduced.
 4. The press durability of the plates decreases.
- Polymeric binders which are water soluble, such as poly(vinyl alcohol), poly(vinyl pyrrolidone),

poly(ethylene oxide), gelatin, casein, etc., are thus unsuitable for use in this invention.

By using core shell particles in which a hydrophobic core is encapsulated by the preferred carboxyl functional shell, colloiddally stable polymer particles can be prepared which are virtually free of water soluble components and thus do not suffer from the disadvantages noted above.

The coating of the radiation sensitive plate is generally water resistant and it is preferred that the plate is produced by applying the core-shell particles to the substrate from wholly or substantially aqueous media. However non-aqueous vehicles and vehicles which are mixtures of aqueous and non-aqueous solvents may be used. In the case where an aqueous vehicle is used, it is preferred that volatile bases such as ammonia or amines are used to solubilise the shell components. The particle size of the core-shell particles is preferably less than 1 micron and more preferably less than 0.5 microns. The weight ratio of shell to core may be in the range of from 1:20 to 20:1 and preferably is in the range of from 1:9 to 1:1.

In an embodiment the source of the high density radiation is a laser operating in the ultra violet, visible or infra-red region of the spectrum. Red and infra-red light emitting lasers are preferred, for example the semiconductor or diode lasers typical of which is the gallium aluminium arsenide laser which operates in the 750-870 nm region.

The radiation-absorbing substance may be present in the same layer as the core-shell particles or it may be incorporated within the particles themselves or it may be present in a separate but adjacent layer. Examples of suitable laser radiation absorbing substances are carbon black and graphite and phthalocyanine, croconium and squarylium type dyestuffs.

The radiation sensitive substance is present in an amount which is effective to cause some coalescence of the particles under the influence of the high intensity radiation. Generally, the radiation sensitive substance will constitute from 2.0 to 80%, by weight, of the coating.

Typical developers for selectively removing the non-coalesced particles, in the non-image areas, are aqueous alkalis such as solutions of ethanalamine, sodium metasilicate, an alkaline phosphate such as sodium phosphate, or an alkali metal hydroxide in water.

The following Examples illustrate the invention.

EXAMPLE 1

414 cm³ of distilled water were placed in a 2L flask equipped with stirrer, condenser, thermometer and N₂ inlet/exit. To the stirred water were added 85.8 cm³ of Carboaset XL37 (a carboxyl functional acrylic resin obtained as a 35% aqueous dispersion from BF Goodrich Ltd). Then 16 cm³ of 25% aqueous ammonia were

added. When a crystal clear solution was obtained, 150g of styrene were added, followed by 1.5g of ammonium persulphate in 10 cm³ distilled water. The mixture was maintained at 65°C with vigorous stirring for a period of four hours to give a final product of solids content 25% w/w, with a particle size of less than 0.5 microns and a residual monomer content of 0.05% w/w. The final product was a core-shell dispersion composed of particles comprising a core of polystyrene and a shell of the carboxylated acrylic copolymer.

150g of Microlith Black C-WA (a carbon black coated with an alkali soluble acrylic resin available from Ciba Geigy) were added to a mixture of 590 cm³ H₂O and 250 cm³ of isopropyl alcohol with stirring. Then 10 cm³ of 25% aqueous ammonia were added and the mixture was stirred for 9 hours. The resultant fine particle size carbon dispersion was filtered through a Whatman GF-D filter paper to give a solids content of 15% w/w.

42 cm³ of the 25% w/w core-shell dispersion and 23.3 g of the 15% w/w carbon dispersion were mixed together and diluted with 120 cm³ of isopropyl alcohol and 14.7 cm³ of distilled water to give 200 cm³ of a 7% w/v dispersion. This was coated on to a grained and anodised aluminium substrate to give a coat weight of 0.6 gm⁻². The resultant radiation-sensitive plate was of very good appearance.

The plate was exposed to the modulated radiation emanating from an array of 100 mW diode lasers outputting at 830 nm to selectively coalesce some of the core-shell particles to form an image. 200 mJ cm⁻² was applied to the plate which was then developed in an aqueous ethanolamine developer (Electrosol 85 of Du Pont-Howson Limited) to give a high resolution developed image. The plate was baked for two minutes at 200°C to give a durable printing plate which was capable of faithfully reproducing more than 90,000 copies.

EXAMPLE 2

The procedure of Example 1 was repeated except that a Nd YAG laser outputting at 1060 nm was used to expose the plate. A similar result was obtained.

EXAMPLE 3

The core shell dispersion from Example 1 was mixed with a squarylium dye (2% of total solids) and coated at 0.6gm⁻² onto an aluminium substrate. Max of the squarylium dye was 800nm in methylene chloride. The plate was exposed, developed and heated as in Example 1. Similar results were obtained.

EXAMPLE 4

110 cm³ of distilled water, 0.34g of ammonium persulphate, and 1.92g of sodium laurylsulphate were

placed in a 500 cm³ flask equipped with stirrer, condenser, thermometer, and N₂ inlet and outlet. The stored solution was heated to 80°C and an emulsion consisting of 83 cm³ styrene, 40 cm³ distilled water, 0.4g ammonium persulphate and 1.1g sodium laurylsulphate was added over 3 hours. The temperature was maintained at between 80 and 85°C. 30 mins after the last of the emulsion had been added a second emulsion containing 22 cm³ butylacrylate, 5 cm³ methacrylic acid, 20 cm³ distilled water 0.5g sodium laurylsulphate, 0.13g ammonium persulphate and 1.8 cm³ octyl mercaptan was added over 1 hour. The temperature was maintained at 80°C for a further 1 hour. On cooling the suspension was filtered through a Whatman GF-D filter paper to remove the small amount of coagulated material. This gave a suspension of solids content 30.5% w/w with particle size of less than 0.3 microns and a monomer content of 0.03% w/w.

15 cm³ of this core-shell dispersion and 9.2 cm³ of the 15% w/w carbon dispersion of Example 1 were mixed together with 1 cm³ of 25% aqueous ammonia, 7 cm³ distilled water and 18 cm³ isopropyl alcohol to give 50 cm³ of a 7% w/v dispersion. This was coated onto a grained and anodised aluminium substrate to give a coat weight of 0.7 gm⁻². This gave a radiation-sensitive plate of similar properties to that described in Example 1.

EXAMPLE 5 (Comparison)

1.42g of Carboset XL37 was diluted with 10 cm³ H₂O and 0.5 cm³ of 25% aqueous ammonia was added to dissolve the polymer. 4.96g of Texicote 53.040 (a 50% w/w solids styrene homopolymer emulsion of MFT 105°C available from Scott Bader) were added, followed by 3.5g of the carbon dispersion of Example 1. The mixture was diluted with 30 ml of isopropyl alcohol and coated on a grained and anodised aluminium substrate to give a coat weight of 0.6 gm⁻². A plate of good appearance was obtained. The plate was imaged using a laser diode but more than 600 mJ cm⁻² was required in order to produce an image which was fully insoluble in the developer used in Example 1.

EXAMPLE 6 (Comparison)

5.96g of Texicote 53-040 were added to 8.25 cm³ of H₂O. 3.5g of the carbon dispersion of Example 1 were added followed by 26 ml of isopropyl alcohol. This was coated on a grained and anodised aluminium substrate at 0.6 gm⁻² to give a plate of acceptable appearance. However, the coating was very poorly adhered to the substrate, being of a dusty texture which was easily removable by, for example, finger contact. The plate imaged and developed (with Electrosol 85) acceptably at an exposure of 200 mJ (laser diodes, outputting at 830nm).

EXAMPLE 7 (Comparison)

Homopolymer styrene emulsions were formed by using of the following surfactants with 100g of styrene using a delayed addition process.

- a. sodium lauryl sulphate (4g)
- b. ammonium laurate (7.5g)
- c. sodium laurate (7.5g)

These emulsions were formulated with Carboset XL37 and carbon dispersion so that the same ratios of polystyrene emulsion: Carboset XL37: carbon dispersion as in Example 5 were obtained. These gave coatings of acceptable appearance at a coat weight of 0.6 gm⁻² on a grained and anodised aluminium substrate. A good image was obtained by diode exposure at 200 mJ followed by developing with Electrosol 85.

The plates were stored in a humidity cabinet at 30°C and 97% RH for 1 week. The plates were very difficult to develop after this time. This is in contrast to the plate of Example 1 which, after imaging at 200 mJ and storing for four weeks in a humidity cabinet, could be readily developed with Electrosol 85.

EXAMPLE 8

Using an identical procedure to that described in Example 1, a styrene-butyl acrylate core-shell polymer was formed. 5 g of the styrene was replaced by 5 g of butyl acrylate. The results were similar to those obtained in Example 1.

EXAMPLE 9

In a 500 ml flask equipped as in Example 1, 43 ml of Carboset XL37 (35% w/w solids) were added to 240 ml of distilled water. The resin was dissolved by adding 6 ml of 25% aqueous ammonia and heating to 50°C. 0.75 g of ammonium persulphate was then added to the mixture, followed by 3.75 g of a mixture of 37.5 g of styrene and 37.5 g of acrylonitrile. After a further 10 minutes, the remainder of the monomer mixture was added over a period of two hours. The temperature was maintained at 60°C for a further four hours and the product was then filtered to give a 20.5% solids dispersion of very fine particle size. This performed in a similar fashion to the material described in Example 1.

EXAMPLE 10 (Comparison)

8g of polyethylene (S394-95, Diamond Shamrock), 2g National 28-29-30 (a terpolymer of vinyl acetate, vinyl versatate and crotonic acid, available from National Adhesives & Resins Ltd), and 1.5g Microlith Black CTA (a predispersed carbon available from Ciba Geigy) were milled in a mixture of toluene, methyl ethyl ketone and methoxy propanol for ten hours. A dispersion of the polyethylene and carbon in

a solution of the alkali soluble resin was obtained. This was coated on a grained and anodised aluminium substrate at 1 gm⁻² to give a plate of good appearance. The plate imaged well at 200 mJ but was so pressure sensitive that development was difficult.

Claims

1. A radiation sensitive plate which comprises a substrate coated with (i) one or more layers each comprising core-shell particles each of which comprises a water-insoluble heat softenable core component (A) and a shell component (B) which is soluble or swellable in aqueous alkaline medium, and (ii) a substance capable of strongly absorbing radiation and transferring the energy thus obtained as heat to the core-shell particles so that at least partial coalescence of the particles occurs.
2. A radiation sensitive plate as claimed in claim 1 wherein the substrate is of metal or plastics material.
3. A radiation sensitive plate as claimed in claim 1 or 2 wherein the core component is an oleophilic film forming addition polymer, polyester, polyamide or polyurethane.
4. A radiation sensitive plate as claimed in claim 3 wherein the addition polymer is derived from styrene, a substituted styrene, an ester of (meth) acrylic acid, a vinyl halide, (meth) acrylonitrile, a vinyl ester or a polyether.
5. A radiation sensitive plate as claimed in any preceding claim wherein the shell component is a polymer containing carboxylic acid or sulphonamido groups.
6. A radiation sensitive plate as claimed in claim 5 wherein the shell component is a copolymer derived from one or more ethylenically unsaturated acids and one or more of styrene, a substituted styrene, an ester of (meth) acrylic acid, (meth) acrylonitrile or vinyl acetate; a dicarboxylic half ester of a hydroxy group containing polymer; or an alkyl or aralkyl half ester of a copolymer of maleic anhydride with styrene or an alkyl vinyl ether.
7. A radiation sensitive plate as claimed in any one of the preceding claims wherein the radiation-absorbing substance is present within said core-shell particles.
8. A radiation sensitive plate as claimed in any one of the preceding claims wherein the radiation-ab-

sorbing substance is carbon black, graphite or a phthalocyanine, croconium or squarylium dye-stuff.

9. A method of forming an image which comprises:- 5

(a) providing a radiation-sensitive plate comprising:-

a substrate provided with a coating comprising 10

(i) one or more layers each comprising core-shell particles each of which comprises a water-insoluble heat-softenable component (A) and a shell component (B) which is soluble or swellable in aqueous alkaline medium, and 15

(ii) a substance capable of strongly absorbing radiation and transferring the energy thus obtained as heat to the core-shell particles so that at least partial coalescence of the particles occurs, 20

(b) image-wise exposing the radiation-sensitive plate to a beam of high intensity radiation, by directing the radiation at sequential areas of the coating and modulating the radiation so that the particles in the coating are selectively at least partially coalesced, and 25

(c) developing the image-wise exposed plate with aqueous alkaline medium to selectively remove the areas containing the non-coalesced particles and leave an image on the substrate resulting from the at least partially coalesced particles. 30

10. A method according to claim 9 wherein the radiation is red or infra-red laser light. 35

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European Patent
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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 9, no. 209 (M-407)(1932) 27 August 1985 & JP-A-60 068 992 (MITSUI) 19 April 1985 * abstract *	1-10	B41M5/36
A	GB-A-2 077 452 (KONISHIROKU) * page 2, line 46 - line 52; claims; examples 1,8 *	1-10	
A	US-A-3 580 719 (E. BRINCKMAN) * the whole document *	1-3	
A	US-A-3 811 773 (M. VRANCKEN) * the whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M B41C G03F
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 25 AUGUST 1992	Examiner STOCK H.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

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